Growth of ZnO thin films exhibiting room-temperature ultraviolet emission by means of atmospheric pressure vapor-phase epitaxy

Kouji Omichi,[a] Kazuhiko Kaiya,[a] Naoyuki Takahashi,*[a] Takato Nakamura,[a] Shinji Okamoto[b] and Hajime Yamamoto[c]

[a]Department of Materials Science and Technology, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatus, Shizuoka 432-8561, Japan.
E-mail: takanao@mat.eng.shizuoka.ac.jp
[b]Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan
[c]Department of Engineering, Tokyo University of Technology, 1404, Katakura, Hachioji, Tokyo 192-8580, Japan

Atmospheric pressure vapor-phase epitaxy of ZnO thin films using ZnI_2 and O_2 as starting materials has been examined: thin films of ZnO deposited onto sapphire (0001) substrates at 1023 K have smooth surfaces free from cracks; the photoluminescence spectra of the ZnO thin film prepared under atmospheric pressure show for the first time an ultraviolet emission centered at 381.0 nm at room temperature.

Wide and direct band-gap semiconductor materials are of considerable interest for applications in optical devices, such as blue and ultraviolet (UV) light-emitting diodes and laser diodes. ZnO, which has been widely used for transparent conductive film varistors, solar cell windows and bulk acoustic wave devices,[1–4] is one of the more promising candidates because it has a direct band-gap of 3.37 eV at room temperature.[5] The key to the room-temperature emission lies in the techniques employed to prepare defect-free ZnO films. This is because oxygen and zinc vacancies, which show a greenish yellow emission, are easily formed. For this reason, a variety of techniques, such as laser molecular beam epitaxy (MBE), RF magnetron sputtering and pulsed laser deposition, have been examined for the preparation of the ZnO films. Zu et al.[6] and Chen et al.[7] have observed an ultraviolet emission at room temperature from ZnO thin films prepared under reduced pressure by laser MBE and plasma-enhanced MBE methods. However, there have been no reports on room-temperature ultraviolet emission from ZnO thin films prepared under atmospheric pressure. In a previous paper, we reported that hexagonal ZnO epitaxial layers can be grown successfully on a sapphire (0001) substrate by atmospheric pressure halide vapor-phase epitaxy (AP-HVPE) using zinc chloride as the starting material. These films showed an emission at 370 nm up to 180 K.[8–10] This communication describes the results of an

investigation into ZnO thin films prepared by AP-HVPE using zinc iodide as the zinc source.

The horizontal quartz reactor used in the present study is the same as that described previously.[8,9] Thin films of ZnO were deposited onto a sapphire (0001) surface in a hot-wall reactor by reaction of ZnI_2 with O_2 under atmospheric pressure. ZnI_2 was evaporated from the source boat at a temperature of 643 K, and then supplied to growth zone. Purified N_2 was used as the carrier gas. Typical growth conditions are summarized in Table 1. As-deposited films were characterized by double crystal X-ray diffraction analysis and atomic force microscopy (AFM). Photoluminescence (PL) spectra were measured by exciting the films with light of 325 nm using a 15 mW He–Cd laser.

The growth rate of the ZnO films obtained under the conditions given in Table 1 was about 0.45 nm s^{-1}. Fig. 1 shows a typical X-ray diffraction profile for the as-grown ZnO films at 1023 K. A strong diffraction line appears at 34.4°, which is assigned to the (0002) diffraction of hexagonal ZnO. This implies that the films were grown epitaxially under atmospheric pressure using ZnI_2 as the zinc source, in analogy with those prepared using $ZnCl_2$.[8–10] The lattice constant was calculated to be $c = 0.5212$ nm utilizing the observed (0002) diffraction, which is slightly larger than a reported value of 0.520661 nm for bulk ZnO crystal.[11] The full width at half-maximum (FWHM) value of the ZnO epitaxial layer is about 1200 s, which is 20% smaller than that of the films deposited by sputtering,[12] while comparable to that of the films deposited by
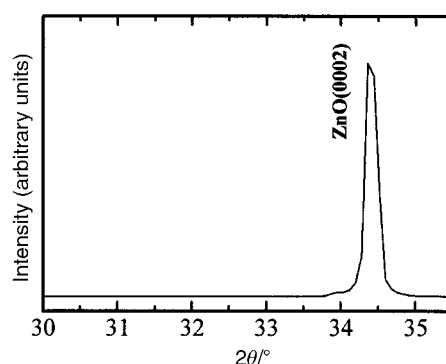
Table 1 Typical growth conditions

Substrate	Sapphire (0001)
ZnI_2 source temperature	643 K
ZnI_2 partial pressure	1.18×10^1 Pa
O_2 partial pressure	3.04×10^5 Pa
Carrier gas	N_2
Total flow rate	1.0×10^{-5} m^3 s^{-1}
Growth temperature	1023 K

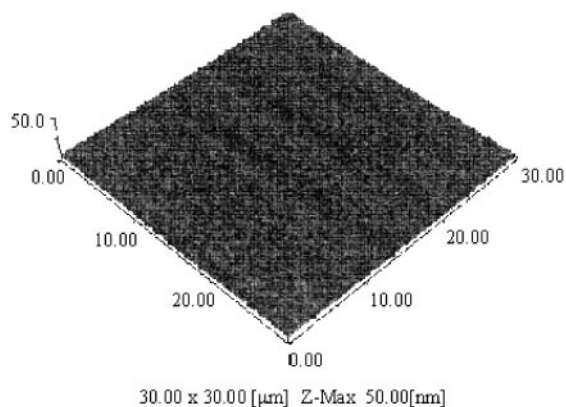**Fig. 1** XRD pattern of an as-grown ZnO film deposited on a sapphire (0001) substrate.
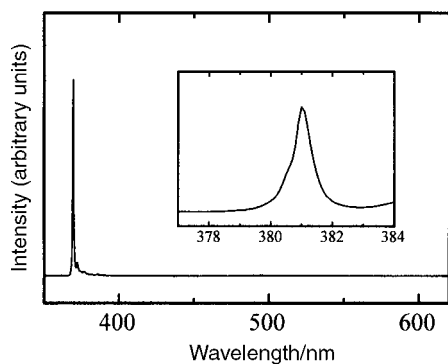
Fig. 2 AFM image of a ZnO epitaxial layer.

Fig. 3 Room-temperature PL signals from a ZnO epitaxial layer.

AP-HVPE using $ZnCl_2$.[8,9] Consequently, it is obvious that the hexagonal ZnO films obtained in this work are of high crystalline quality.

A representative AFM image of the high-quality ZnO film is shown in Fig. 2. The mean square roughness (R_{ms}) for $30 \times 30 \ \mu m^2$ of the ZnO film is less than 7 nm, suggesting that the surface is flat and smooth. Also, it was found that the surface morphology is smoother than that of ZnO films prepared on sapphire (0001) by CVD.[13]

A room-temperature PL spectrum of the ZnO film is shown in Fig. 3. It is worth noting that only an emission appearing at 381.0 nm is observed in the ultraviolet region, with no emission occurring in the visible region. This implies that the epitaxial ZnO film growns by AP-HVPE using $ZnCl_2$ are of excellent optical quality. Furthermore, they have no deep-level impurities and/or lattice defects in them. As a consequence, it is concluded that epitaxial ZnO films exhibiting room-temperature ultraviolet emission were successfully grown by means of atmospheric pressure vapor-phase growth.

Acknowledgements

Notes and references

1 T. L. Yang, D. H. Zhang, J. Ma, H. L. Ma and Y. Chen, *Thin Solid Films*, 1998, **326**, 60.
2 J. F. Cordaro, Y. Shim and J. E. May, *J. Appl. Phys.*, 1986, **60**, 4186.
3 B. Sang, A. Yamada and M. Konagai, *Jpn. J. Appl. Phys.*, 1998, **37**, L206.
4 P. Verardi, N. Nastase, C. Gherasim, C. Ghica, M. Dinescu, R. Dinu and C. Flueraru, *J. Cryst. Growth*, 1999, **197**, 523.
5 C. Klingshirn, *Phys. Status Solidi B*, 1975, **71**, 547.
6 P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma and Y. Segawa, *J. Solid State Commun.*, 1997, **103**, 459.
7 Y. Chen, D. M. Bagnall, Z. Zhu, T. Sekiuchi, K. Park, K. Hiraga, T. Yao, S. Koyama, M. Y. Shen and T. Goto, *J. Cryst. Growth*, 1997, **181**, 165.
8 N. Takahashi, K. Kaiya, T. Nakamura, Y. Momose and H. Yamamoto, *Jpn. J. Appl. Phys.*, 1999, **38**, L454.
9 N. Takahashi, K. Kaiya, K. Omichi, T. Nakamura, S. Okamaoto and H. Yamamoto, *J. Cryst. Growth*, 2000, **209**, 822.
10 K. Kaiya, K. Omichi, N. Takahashi, T. Nakamura, S. Okamoto and H. Yamamoto, *J. Mater. Chem.*, 2000, **10**, 969.
11 JCPDS File no. 36-1451, 1990.
12 M. Kadota and M. Minakata, *Jpn. J. Appl. Phys.*, 1998, **37**, 2929.
13 T. Shiosaki, S. Ohnishi and A. Kawabata, *J. Appl. Phys.*, 1979, **50**, 3113.